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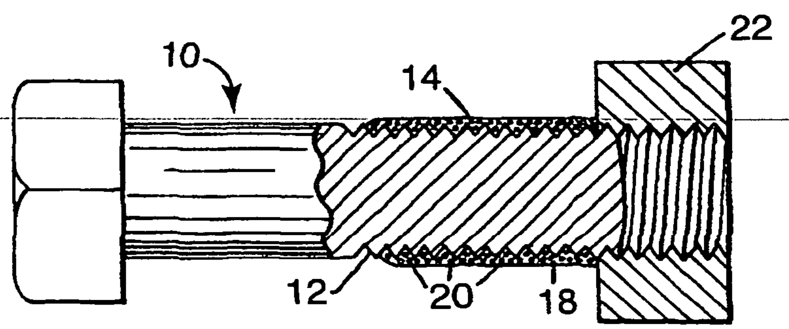

(57) Abstract: Humidity resistant, water-based adhesive compositions are disclosed. The adhesive compositions include epoxy capsules, a non-volatile amine curative, and a binder system that has at least one water-insoluble polymer. The epoxy capsules contain an outer shell material and encapsulated epoxy resin within the outer shell material. The adhesives are suitable for use in a number of applications, including as a coating on screws and bolts. Methods of making and using the adhesives are also disclosed.

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HUMIDITY RESISTANT WATER-BASED ADHESIVE COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Patent Application No. 60/390,640, filed June 21, 2002.

FIELD OF THE INVENTION

The present invention relates to humidity resistant, water-based adhesives and methods of making such adhesives. The present invention further relates to articles of manufacture that include a substrate coated with a humidity resistant, water-based adhesive.

BACKGROUND OF THE INVENTION

For over thirty years, adhesives have been used to coat mechanical fasteners (i.e., screws, bolts, nuts, pipe joints, threaded nails, etc.), which are attached to a desired substrate. The term "fastener adhesives" has been used to describe such adhesive compositions. Typically, fastener adhesives containing a microencapsulated epoxy resin, an amine curative, and an organic binder are used to coat at least a portion of the mechanical fastener, such as the threads of a screw. In these adhesive systems, the epoxy resin is separated from the amine curative (by encapsulating the epoxy resin) to prevent premature curing of the adhesive composition until use. During the process of attaching the coated mechanical fastener (e.g., screwing a screw or bolt into a desired object), the microcapsules are crushed, causing the epoxy resin and the amine curative to mix, resulting in an activated adhesive. The activated adhesive composition typically cures over a period of several days. However, the rate of cure can be accelerated by heating.

SUMMARY OF THE INVENTION

The present invention is directed to a water-based adhesive composition that can have improved humidity resistance. The water-based adhesive composition contains epoxy capsules, a non-volatile amine curative, and a binder resin system that includes at least one water insoluble polymer. The epoxy capsules include an outer shell material and an epoxy resin encapsulated within the outer shell material (i.e., the shell material surrounds the encapsulated material). The adhesive composition of the present invention may be used in a variety of applications including, but not limited to, coatings for mechanical fasteners (i.e., as fastener or threadlocking adhesives).

The present invention is further directed to articles of manufacture comprising a substrate such as a mechanical fastener having a water-based adhesive

coated thereon, wherein the water-based adhesive comprises epoxy capsules, a non-volatile amine curative, and a binder resin system that includes at least one water insoluble polymer. The epoxy capsules include an outer shell material and an epoxy resin encapsulated within the outer shell material. The mechanical fastener of the present invention often exhibits improved humidity resistance. Some of the articles may be stored for a period of up to one year without negatively impacting the adhesive coating thereon.

The present invention is further directed to a method of making a water-based adhesive composition that can have improved humidity resistance. The method comprises the steps of mixing water with microencapsulated epoxy resin in the form of epoxy capsules, a non-volatile amine curative, and a binder resin that includes at least one water insoluble polymer. The present invention is also directed to a method of making an article such as mechanical fasteners comprising the step of coating the article with a water-based adhesive composition.

These and other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention is further described with reference to the appended figures, wherein:

FIG. 1 is a cross-sectional view of a coated mechanical fastener of the present invention;

FIG. 2 is a photograph of exemplary epoxy capsules for use in present invention viewed using a Scanning Electron Microscopy at 150X magnification; and

FIG. 3 is a graphical display of an exemplary particle size distribution for a sample of epoxy capsules suitable for use in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a water-based adhesive composition that can have improved humidity resistance. The adhesive composition comprises epoxy capsules, a non-volatile amine curative, and a binder resin that includes at least one water insoluble polymer. The epoxy capsules include an outer shell material and an epoxy resin encapsulated within the outer shell material. The adhesive composition may further contain one or more optional materials such as fillers, cross-linking agents, and thickeners. The water-based adhesive compositions of the present invention may be used in applications where resistance is a consideration, such as in applications wherein the adhesive is exposed to the environment and stored prior to use.

The present invention is also directed to various articles of manufacture comprising a substrate coated with a water-based adhesive composition. In particular, the present invention is directed to mechanical fasteners, such as screws, bolts, nuts, pipe joints, and nails, which are coated with an adhesive composition. The adhesive compositions are often humidity resistant.

A variety of materials may be used to form the adhesive compositions of the present invention. A description of materials suitable for use in the present invention is given below.

I. Adhesive Composition Components

The following materials may be used to form the water-based adhesive compositions of the present invention: epoxy capsules, curatives, binder resins, optional cross-linking agents, optional fillers, optional thickeners, optional additives, and water. The compositions can be a one-part or a two-part composition. As used herein, the term "one-part" refers to an adhesive composition where the epoxy capsules are mixed with the curative prior to use. As used herein, the term "two-part" refers to an adhesive composition where the epoxy capsules are stored in a separate container from the curative prior to use; the epoxy capsules and curative is mixed at the time of use.

A. Epoxy Capsules

The adhesive composition of the present invention comprises one or more microencapsulated epoxy resins (herein referred to as "epoxy capsules"). Epoxy capsules comprise an outer shell material (i.e., the encapsulating material) and an encapsulated material within the outer shell material. The encapsulated material includes an epoxy resin. A description of the encapsulating material and encapsulated material is given below.

i. Encapsulating Material

A variety of encapsulating materials may be used in the present invention to form the outer shell of the epoxy capsules. Suitable encapsulating materials include, but are not limited to, cross-linked resin materials or polymers formed by reacting formaldehyde with urea, melamine, or a combination thereof. In some applications, the encapsulating material comprises a urea-formaldehyde-melamine material. The urea-formaldehyde-melamine material, for example, may comprise from about 20 to about 50 weight percent (wt-%) urea, from about 30 to about 70 wt-% formaldehyde, and from about 3 to about 30 wt-% melamine, wherein each wt-% is based on the total weight of the urea-formaldehyde-melamine encapsulating material. The urea-formaldehyde-melamine material may comprise from about 35 to about 50 wt-% or from about 40 to about 50 wt-% urea, from about 40 to about 60 wt-% or from about 45 to about 55 wt-% formaldehyde, and from about 5 to about 15 wt-

% or from about 5 to about 10 wt-% melamine. In a specific example, the encapsulating material can comprise a urea-formaldehyde-melamine material containing about 42 to about 46 wt-% urea, about 46 to about 50 wt-% formaldehyde, and about 6 to about 10 wt. % melamine.

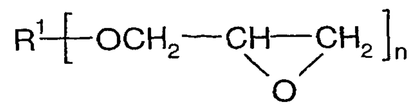
Formation of the encapsulating material and the epoxy capsules may be carried out using any microencapsulation technique known in the art. One desired method of preparing the epoxy capsules of the present invention may be found in Example 1 below. Other microencapsulation techniques that are known in the art can be used to prepare the epoxy capsules.

ii. Encapsulated material

The encapsulated material includes one or more epoxy resins. Epoxy resins suitable for use in the present invention may be any organic compound having at least one oxirane ring that is polymerizable by a ring opening reaction. These materials generally have, on average, at least two oxirane rings per molecule and may also be referred to as "polyepoxides" or "epoxides." The "average" number of epoxy groups per molecule is defined as the number of epoxy groups in the epoxy resin divided by the total number of epoxy molecules present. Such materials include both monomeric and polymeric epoxides and may be, for example, aliphatic, alicyclic, heterocyclic, cycloaliphatic, or aromatic and may further be combinations thereof. Epoxides may be liquid or solid or blends thereof, blends being especially useful in providing tacky adhesive films. The polymeric epoxides include, but are not limited to, linear polymers having terminal epoxy groups (for example, a diglycidyl ether of a polyoxyalkylene glycol), polymers having skeletal oxirane units (for example, polybutadiene polyepoxide), and polymers having pendent epoxy groups (for example, a glycidyl methacrylate polymer or copolymer). The molecular weight of the epoxy resin may vary from about 74 to about 100,000 or more. Mixtures of various epoxy resins may also be used in the adhesive compositions of the present invention.

Suitable epoxy resins for use in the present invention include, but are not limited to, epoxy resins that contain cyclohexene oxide groups such as the epoxycyclohexane carboxylates, typified by 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 3,4-epoxy-2-methylcyclohexylmethyl-3,4-epoxy-2-methylcyclohexane carboxylate, and bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate. For a more detailed list of useful epoxides of this nature, reference may be made to U.S. Patent No. 3,117,099, the disclosure of which is incorporated herein by reference.

Other epoxy resins, which are particularly suitable for use in the present invention, include glycidyl ether monomers and have a structure as shown below:



where R' is aliphatic, such as an alkyl group, aromatic, such as an aryl group, or combinations thereof; and n is an integer from about 1 to about 6. Examples of epoxy resins having a structure as shown above include, but are not limited to, the glycidyl ethers of polyhydric phenols obtained by reacting a polyhydric phenol with an excess of chlorohydrin such as epichlorohydrin, for example, the diglycidyl ether of 2,2-bis-(4-hydroxyphenol)propane (Bisphenol A). Further examples of epoxides of this type are described in U.S. Patents Nos. 3,642,937 and 3,746,068, both of which are assigned to 3M Company (St. Paul, MN), the disclosures of which are incorporated herein by reference.

A number of commercially available epoxy resins may be used in the present invention. Epoxides, which are readily available, include, but are not limited to, octadecylene oxide; epichlorohydrin; styrene oxide; vinylcyclohexene oxide; glycidol; glycidyl methacrylate; diglycidyl ether of Bisphenol A containing materials (for example, those available under the trade designations "EPON™ 815C", "EPON™ 813", "EPON™ 828", "EPON™ 1004", and "EPON™ 1001F" from Resolution Performance Products, Houston, TX); diglycidyl ether of bisphenol F (for example, those available under the trade designations "ARALDITE™ GY281" from Ciba Specialty Chemicals Holding Company, Basel, Switzerland, and "EPON™ 862" from Resolution Performance Products); vinylcyclohexane dioxide (for example, one available under the trade designation "ERL-4206" from Dow Chemical Co., Midland, MI); 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexene carboxylate (for example, one available under the trade designation "ERL-4221" from Dow Chemical Co., Midland, MI); 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy) cyclohexane-metadioxane (for example, one available under the trade designation "ERL-4234" from Dow Chemical Co.); bis(3,4-epoxycyclohexyl) adipate (for example, one available under the trade designation "ERL-4299" from Dow Chemical Co.); dipentene dioxide (for example, one available under the trade designation "ERL-4269" from Dow Chemical Corp.); epoxidized polybutadiene (for example, one available under the trade designation "OXIRON™ 2001" from FMC Corp., Chicago, IL); epoxy silanes (for example, beta-3,4-epoxycyclohexylethyltrimethoxy silane and gamma-glycidoxypropyltrimethoxy silane, commercially available from Dow Chemical Co.); flame retardant epoxy resins (for example, one available under the trade designation "DER-542", a brominated bisphenol type epoxy resin available from Dow Chemical Co.); 1,4-butanediol diglycidyl ether (for example, one available under the trade designation

"ARALDITE™ RD-2" from Ciba Specialty Chemicals); hydrogenated bisphenol A-epichlorohydrin based epoxy resins (for example, one available under the trade designation "EPONEX™ 1510" from Resolution Performance Products); and polyglycidyl ether of phenol-formaldehyde novolak (for example, one available under the trade designation "DEN-431" and "DEN-438" from Dow Chemical Co.).

The encapsulated material can include epoxy resin mixed with an optional epoxy diluent. The epoxy diluent is often added to lower the viscosity of the epoxy resin. The epoxy diluent is selected to be compatible with the epoxy resin and typically has low solubility in the water phase. The epoxy diluent typically contains one epoxy group per molecule. Suitable materials include, for example, n-butyl glycidyl ether, o-cresyl glycidyl ether, and materials similar to those found in the HELOXY™ Epoxy Resin Modifiers product family (Resolution Performance Products).

In one specific application, the encapsulated material is EPON 815C™, a mixture of Bisphenol A diglycidyl ether and n-butyl glycidyl ether. In yet another specific application, the encapsulated material is EPON 813™, a mixture of Bisphenol A diglycidyl ether and o-cresyl glycidyl ether.

The epoxy capsules may also contain other encapsulated materials. Suitable additional encapsulated materials for use in the epoxy capsules include, but are not limited to, solvents and plasticizers. Addition of these materials to the epoxy resin may be necessary to lower the viscosity of the organic phase to the appropriate range for the microencapsulation process.

iv. Exemplary Capsule Composition and Dimensions

In some embodiments, the epoxy capsules used in the adhesive compositions of the present invention are capsules as described in Example 1 comprising a urea-formaldehyde-melamine shell with epoxy resin that includes a diglycidyl ether of Bisphenol A (e.g., EPON™ 815C or EPON™ 813). Suitable epoxy capsules typically include, for example, about 70 to about 95 wt-% epoxy resin and about 5 to about 30 wt-% encapsulating material based on the weight of the epoxy capsules. In some embodiments, the epoxy capsules include about 75 to about 90 wt-% or about 80 to about 90 wt-% of the epoxy resin and about 10 to about 25 wt-% or about 10 to about 20 wt-% encapsulating material.

The adhesive composition can include from about 20 to about 60 wt-% capsules, from about 30 to about 50 wt-% capsules, or from about 35 to about 40 wt-% capsules based on the total weight of the adhesive composition.

Exemplary epoxy capsules suitable for use in the present invention are shown in FIG. 2. The epoxy capsules shown in FIG. 2 were photographed using a Scanning Electron Microscopy at 150X magnification. As shown in FIG. 2, the epoxy

capsules may be present as a single capsule **21**, as a cluster of capsules **22**, or as a combination thereof.

The capsules used in the adhesive compositions may have a size and shape that varies depending upon the desired use of the adhesive composition. In general, the encapsulation process produces capsules with a size distribution, or range of capsule sizes. The size distribution can be measured by Laser Light Scattering and is typically a normal, or almost normal, distribution of the capsule diameters. One way to describe the capsule size distribution is by a median (i.e., middle value of the distribution). The capsules often have a spherical shape and a median particle diameter of up to about 40, up to about 60, up to about 80, up to about 100, or up to about 120 micrometers. For example, the capsules can have a spherical shape and a median particle diameter ranging from about 20 micrometers to about 120 micrometers, from about 25 micrometers to about 100 micrometers, or about 30 to about 70.

The epoxy capsules can be characterized by their particle size distribution. Ninety percent of the capsules typically have a diameter greater than about 10 micrometers. In some embodiments, ninety percent of the capsules have a diameter greater than about 15 micrometers, about 20 micrometers, about 30 micrometers, about 40 micrometers, about 50 micrometers, or about 60 micrometers. Ninety percent of the capsules have a diameter less than about 220 micrometers. In some embodiments, ninety percent of the capsules have a diameter less than about 200 micrometers, about 160 micrometers, about 140 micrometers, about 120 micrometers, about 100 micrometers, or about 80 micrometers.

For example, in some exemplary epoxy capsules, at least 80 percent of the capsules are in the size range of about 15 to about 80 micrometers with a median diameter of about 30 to about 40 micrometers. In other exemplary epoxy capsules, at least about 80 percent of the capsules are in the size range of about 15 to about 140 micrometers with a median diameter of about 50 to about 60 micrometers.

One exemplary particle size distribution for a sample of epoxy capsules suitable for use in present invention is shown in FIG. 3. A median diameter of 36 micrometers is shown at peak **31** in FIG. 3.

B. Curatives

The adhesive composition of the present invention may also contain one or more non-volatile, water-soluble or water-dispersible amine curatives. In some embodiments, the amine curatives are film-forming materials (i.e., a film forms when the amine curative is mixed with the epoxy capsules and the solvent or water is removed).

Suitable curatives for use in the present invention include, but are not limited to, non-volatile amine curatives found in U.S. Patent No. 3,642,937, such as imidazole; 1,3-dipiperidylpropane; 1,6-hexane diamine; 1,8-octane diamine; 1,10-decane diamine; 4,4'-methylenedianiline; substituted alkylene diamines; polyamide resins such as the VERSAMID series of resins (a dimerized unsaturated fatty acid reacted with alkylene diamines) available from Cognis Corporation, Cincinnati, OH; and epoxy-imidazole adducts, as described in U.S. Patent Nos. 3,756,984; 5,717,011; 5,798,399; 5,801,218; and 5,733,954 incorporated herein by reference.

Useful commercially available amine curatives include, but are not limited to, modified aliphatic amines such as ANCAMINE™ 2014AS, 2014FG, 2337S, and 2441 (Air Products and Chemicals, Allentown, PA); ANCAMINE™ 1770 and 2049 cycloaliphatic amines (Air Products and Chemicals, Allentown, PA); AMICURE™ CG-1200, CG-1400, CG-325, and CG-NA dicyandiamide (Air Products and Chemicals, Allentown, PA); CUREZOL™ 2MZ-AZINE, 2,4-diamino-6(2'methylimidazoleyl-(1'))ethyl-s-triazine and other imidizoles such as CUREZOL™ AMI-2, 2E4MZ, 1B2MZ, 2PZ, C17Z, 2PHZ-S, and 2MA-OK curatives (Air Products and Chemicals, Allentown, PA); EPI-CURE™ 8290-Y-60, 8295-H-60, 8535-W-50, 8536-MY-60, 8540-MU-60, 8537-WY-60 (Resolution Performance Products, Houston, TX); polyamidoamines such as ANQUAMINE™ 360, 401, 419, 456, and 701 (Air Products and Chemicals, Allentown, PA); LUPASOL™ polyethylenimine polymers such as FG, PR 8515, Waterfree, P, PS (BASF Corporation, Resselaer, NY); CORCAT™ polyethylenimine polymers such as P-600 (EIT Company, Lake Wylie, SC); and polyoxyalkyleneamines such as JEFFAMINE™ D-230, D-400, D-2000, HK-511 (XTJ-511), XTJ-510 (D-4000), XTJ-500 (ED-600), XTJ-502 (ED-2003), T-403, XTJ-509 (T-3000), and T-5000 (Huntsman Corporation, Houston, TX).

In some embodiments, the amine curatives are polymeric. For example, the adhesive composition can contain one or more amine curatives selected from ANQUAMINE™ 401, ANQUAMINE™ 701, LUPASOL™ PS, and CORCAT™ P-600.

The adhesive composition of the present invention may comprise one or more amine curatives in an amount, which varies depending on the particular curative used, and the desired properties and use of the resulting composition. The adhesive composition often comprises up to 40 wt-%, up to 30 wt-%, or up to about 20 wt-%. For example, the adhesive composition can contain from about 1 to about 40 wt-%, from about 2 to about 30 wt-%, from about 5 to about 25 wt-%, or from about 15 to about 20 wt-% of one or more amine curatives, based on the total wet weight of the adhesive composition.

C. Binder Resins

It can be advantageous to use water-based polymer dispersions as binder resins in the present invention because water-based polymer dispersions often provide performance similar to that obtained from conventional solvent-based resins. In addition, water-based polymer dispersions have low volatiles and thus can be more environmentally friendly than solvent-based coatings.

The term "dispersion" encompasses any solid dispersed in a liquid medium including, for example, latexes, emulsions, colloidal suspensions, and the like. A latex is a dispersion of water-insoluble polymer particles in water, generally made by emulsion polymerization (Organic Coatings: Science and Technology, Wicks et al., John Wiley & Sons, (1972) p. 64). The molecular weights of latex polymers are usually high and typically greater than 1,000,000; however, the high molecular weight of the latex polymer does not affect the viscosity of the latex, making it possible to formulate relatively high solids coatings with good film properties. The use of water-based polymer dispersions is particularly desirable because they are made from water-insoluble thermoplastic polymers with excellent water, humidity and chemical resistance. The wide range of polymer dispersions offers a formulator considerable latitude to achieve the desired properties of the adhesive or coating.

The term "water-dispersed" means that the carrier is primarily water, However, incidental organic solvents, such as those present in additives and commercially available components, may be present. Thus, the adhesive compositions of the present invention are at least substantially free of organic solvents (e.g., no more than about 5 wt-%, no more than about 3 wt-%, no more than about 2 wt-%, or no more than about 1-wt% organic solvent based on the weight of the adhesive composition). In many applications, however, "water-dispersed" refers to a 100% water carrier.

For these reasons, the adhesive composition of the present invention may also contain one or more polymer dispersions of thermoplastic binder resins. Choice of binder resins is dependent on compatibility with the adhesive components, in particular the epoxy capsules and curative. Suitable binder resins include, but are not limited to, ethylene-vinyl acetate (EVA) copolymer emulsions, ethylene-vinyl chloride copolymer emulsions, vinyl acetate-ethylene-vinyl chloride copolymer emulsions, acrylate-vinyl acetate-ethylene copolymer emulsions, vinyl acrylic emulsions, acrylic emulsions, vinyl acetate-acrylic copolymer emulsions, styrene-acrylic copolymer emulsions, vinyl chloride-vinyl acetate-ethylene terpolymer emulsions, vinyl acetate homopolymer emulsions, polyester dispersions, polyurethane dispersions, acrylic-urethane dispersions, butadiene dispersions, and butadiene-styrene copolymer dispersions.

Examples of commercially available vinyl acetate-ethylene copolymer dispersions suitable for use in the present invention include, but are not limited to, AIRFLEX™ 105, 108, 109, 124, 128, 300, 320, 400, 401, 405,410, 420, 426, 440, 460, 465, 500BP, 525BP, 526BP, 528BP, 530BP, 531BP, 532BP, 533BP, 562BP, 720BP, 7200 (Air Products, Inc., Philadelphia, PA). An example of a commercially available vinyl acetate-ethylene-vinyl chloride copolymer emulsion suitable for use in the present invention includes, but is not limited to, AIRFLEX™ 742BP (Air Products, Inc., Philadelphia, PA). Examples of commercially available ethylene-vinyl chloride copolymer emulsions or vinyl chloride-vinyl acetate-ethylene terpolymer emulsions suitable for use in the present invention include, but are not limited to, AIRFLEX™ 430, 451BP, 4500, 4514, 4530; VANCRYL™ 600, 605, 610; (all from Air Products, Inc., Philadelphia, PA).

An example of commercially available acrylate-vinyl acetate-ethylene emulsion suitable for use in the present invention includes, but is not limited to, AIRFLEX™ 600BP (Air Products, Inc., Philadelphia, PA). An exemplary commercially available vinyl acetate-acrylic copolymer emulsion is FLEXBOND 325 (Air Products, Inc., Philadelphia, PA). Examples of commercially available acrylic emulsions suitable for use in the present invention include, but are not limited to, AIRBOND™ ACP67, ACP625 (Air Products, Inc., Philadelphia, PA). Examples of commercially available vinyl acrylic emulsions suitable for use in the present invention include, but are not limited to, FLEXBOND™ F82BP (Air Products, Inc., Philadelphia, PA). Examples of commercially available styrene acrylic emulsions suitable for use in the present invention include, but are not limited to, VANCRYL™ 937, 960, 989 (Air Products, Inc., Philadelphia, PA) and CARBOSET CR-760 (Noveon, Inc., Cleveland, OH). Examples of commercially available vinyl acetate emulsions suitable for use in the present invention include, but are not limited to, VINAC™ 285, 521, 523, 524 (Air Products, Inc., Philadelphia, PA). Examples of commercially available acrylic-urethane dispersions suitable for use in the present invention include, but are not limited to, HYBRIDUR™ 570; and FLEXTHANE™ 620, 630 (all from Air Products, Inc., Philadelphia, PA). Examples of commercially available polyurethane dispersions suitable for use in the present invention include, but are not limited to, WITCOBOND™ products available from Uniroyal Chemical Company, Middlebury, CT, such as WITCOBOND™ W-232, W-506, W-253 and W-320 and BAYHYDROL 121 (Bayer, Pittsburgh, PA). In some compositions that include a polyurethane, the polyurethane is a non-ionic dispersion such as WITCOBOND™ W-320. Examples of commercially available butadiene-containing emulsions suitable for use in the present invention include, but are not limited to HYCAR™ Butadiene Emulsions 1561, 1552, 1562, 1571, 1572, 1577, 1578x1 and 1581 (BF Goodrich, Cleveland, OH); or GOOD-

RITE™ Styrene-Butadiene Emulsions such as SB-0738, SB-1170 and SB-0706 (BF Goodrich, Cleveland, OH). Examples of commercially available polyester dispersions include, but are not limited to, SANCURE 1601 (Noveon, Inc., Cleveland, OH).

The adhesive composition of the present invention may contain one or more binder resin materials selected from the materials above. In some embodiments, the binder resin material includes one or more materials selected from ethylene-vinyl acetates, polyurethanes, and butadiene-containing polymers. For example, the adhesive composition can contain a mixture of ethylene-vinyl acetates and polyurethanes. The polyurethane can be a non-ionic dispersion.

The adhesive composition of the present invention contains at least 0.1 wt-%, at least about 0.5 wt-%, at least about 5 wt-%, or at least 10 wt-% of the above-described binder resin. The adhesive compositions typically contain up to about 35 wt-%, up to about 30 wt-%, up to about 25 wt-%, or up to about 20 wt-% of the above-described binder resins. For example, the adhesive composition of the present invention can contain about 5 to about 25 wt-% or about 10 to about 20 wt-% of one or more of the above-described binder resins.

D. Optional Cross-linking Agents

Adhesive compositions of the present invention may also contain one or more optional cross-linking agents to enhance the tensile strength or chemical resistance of the adhesive coating. Suitable cross-linking agents are those that are compatible with the adhesive component, particularly the epoxy capsules and curative. Cross-linking agents include, but are not limited to, water-based zinc oxide dispersions such as OCTOCURE 462, and combinations of zinc compound and sulfur compound dispersions such as OCTOCURE 590 and T2000. These materials are known as rubber accelerators, vulcanizates and stabilizers, and act to improve coating properties by cross-linking the thermoplastic binder resins.

OCTOCURE 462 is an aqueous dispersion of zinc oxide having a surface area of 8 to 10 m^2/g. OCTOCURE 462 has the following physical properties: solids content of about 60 to 62%; a pH of about 9 to 11; a viscosity of about 1000 to 3000 cps; and an average particle size of less than about 5 micrometers.

OCTOCURE 590 is a composite mixture of ingredients, which accelerates vulcanization of latex compounds. This composite mixture contains curatives, accelerators, antioxidants, and colloidal stabilizers in the following ratio of active parts: zinc oxide - 2.00 parts; sulfur - 1.65 parts; ZMBT (zinc mercaptobenzothiazole) - 0.50 parts; ZDE (zinc diethyldithiocarbamate) - 1.00 parts; and an antioxidant - 0.75 parts. OCTOCURE 590 has the following physical

properties: solids content of about 59 to 61%; a pH of about 9 to 10; a viscosity of about 1000 to 3000 cps; and an average particle size of less than about 10 micrometers.

Another class of cross-linking agents is the polyfunctional aziridines, described in U.S. Patent No. 5,783,303 the disclosure of which is hereby incorporated by reference. Suitable, commercially available polyfunctional aziridines are available under the trade designations "XAMA-2" and "XAMA-7" (B. F. Goodrich Chemical Co., Cleveland, OH), and "CROSSLINKER CX-100" (Neoresins, a business unit of Avecia, Wilmington, MA).

Another method of cross-linking the adhesive composition is by addition of a small amount of water-dispersed epoxy resin to the adhesive composition, such that the curative is present in excess of the water-dispersed epoxy resin. The water-dispersed epoxy resin can react with a small amount of the amine curative and thereby improve the physical properties of the adhesive coating. It is desirable that the amine curative is not used up in the reaction with the water-dispersed epoxy resin, so that excess amine curative reacts with the epoxy in the capsules when the capsules are broken open. Addition of the water-dispersed epoxy resin is particularly useful if the adhesive is delivered in a two-part format, where the curative is separate from the epoxy capsules. The water dispersed epoxy resin can be added to the adhesive component containing the epoxy capsules and is not reacted until mixing with the curative. Examples of commercially available water-dispersed epoxy resins suitable for use in the present invention include, but are not limited to, ANCAREZ™ AR550 (Air Products, Inc., Philadelphia, PA) and EPI-REZ™ Resins 3515-W-60, 3515-W-50, 3519-W-50, 3522-W-60 (Resolution Performance Products, Houston, TX).

The adhesive composition can contain up to about 5 wt-% of one or more of the above-described cross-linking agents. For example, the adhesive composition can contain from about 0.05 wt-% to about 5 wt-% of one or more cross-linking agents. In some embodiments, the adhesive composition can contain from about 0.5 to 3.0 wt-% of one more cross-linking agents.

E. Water

Adhesive compositions of the present invention also include water as a dispersing agent and viscosity modifier. The adhesive composition of the present invention desirably contains from about 10.0 wt-% to about 80.0 wt-% water. For example, the adhesive composition can contain from about 10.0 wt-% to about 50.0 wt-% water, or from about 10.0 wt-% to about 20 wt-% water, based on a total weight of the adhesive composition.

F. Optional Fillers

Adhesive compositions of the present invention may also contain one or more inorganic filler materials or polymeric filler materials.

Suitable inorganic filler materials are described in Organic Coatings: Science and Technology, Wicks et al., John Wiley & Sons, (1972) p. 318-321. These fillers can include, but are not limited to, titanium dioxide, calcium carbonate, mica (aluminum potassium silicate), kaolin clays, talc (magnesium silicate), silicon dioxide, diatomaceous (Fuller's) earth, iron oxide, Wollastonite, zeospheres, zinc chromate, zinc phosphate, zinc oxide, barium sulfate, or combinations thereof. In some embodiments, the filler material includes titanium dioxide, mica, and calcium carbonate. In other embodiments, the filler material includes a mixture of titanium dioxide and mica.

Suitable polymeric filler materials include, for example, polyethylene, polytetrafluoroethylene, and the like. The polymeric filler material can be a powder, a fiber, or a combination thereof.

The adhesive composition of the present invention may contain up to about 30 wt-% of one or more of the above-described inorganic or polymeric filler materials based on a total weight of the adhesive composition. In some embodiments, the adhesive composition of the present invention contains from about 15 wt-% to about 20 wt-% of the above-described inorganic or polymeric filler materials based on a total weight of the adhesive composition.

G. Optional Thickeners

One or more optional thickeners may be used in the curable coating compositions of the present invention to increase the viscosity of the dispersions. It can be advantageous to increase the viscosity of the liquid adhesive such that the epoxy capsules and fillers stay suspended and do not settle to the bottom of the container. Thickeners also can improve the adhesive coating properties by providing coatings that do not sag. Suitable thickeners are those that are compatible with the adhesive components. As used herein, "compatible" means that the thickener does not cause adverse affects to the curable composition (e.g., precipitation, flocculation, or other separation of the components), or to the cured coating (e.g., disruption of film continuity, phase separation, or loss of adhesion to the backing).

Typical organic thickeners for use in the adhesive compositions of the present invention are associative thickeners. An "associative" thickener is a polymeric compound having hydrophobic groups that associate with each other or with the dispersed polymer particles of the curable coating composition. Examples of preferred thickeners are the non-ionic polyurethanes ACRYSOL™ RM-825, RM-8W, RM-1020, RM-2020NPR, RM-12W and SCT-275 (Rohm & Haas, Philadelphia PA). An

associative thickener, or mixture of associative thickeners, can be present in the adhesive compositions of the present invention in an amount effective to increase the viscosity of the adhesive such that the epoxy capsules and filler stay suspended and to provide coatings that do not sag. Preferably, an associative thickener, or mixture of associative thickeners, is present in the adhesive compositions of the present invention in an amount of less than about 1 wt-%. For example, the associative thickener can be present in an amount of about 0.05-0.8 wt-%, based on the total weight of the adhesive composition.

Inorganic thickeners for use in the adhesive compositions of the present invention include, but are not limited to, metallic oxides, such as aluminum oxide silicon dioxide, and attapulgite clays. In some embodiments, the inorganic thickeners are aluminum oxide and attapulgite clay. For example, aluminum oxide can be present in the A-side (i.e., amine side) of a two part adhesive compositions in an amount of less than about 1 wt-% (e.g., in an amount of about 0.05-0.8 wt-%) based on the total weight of the adhesive composition. In other embodiments, attapulgite clay thickener is present in the B-side (i.e., epoxy side) of a two part adhesive compositions in an amount of less than about 0.5 wt-% (e.g., in an amount of about 0.05-0.3 wt-%) based on the total weight of the adhesive composition.

H. Other Additives

The adhesive composition may contain up to about 50 wt-%, desirably, up to about 10 wt-%, of various additives such as stabilizers, antioxidants, plasticizers, surfactants, defoamers, tackifiers, flow control agents, cure rate retarders, adhesion promoters (for example, silanes and titanates), adjuvants, flattening agents, UV absorbers, UV scavengers, impact modifiers, expandable microspheres, thermally conductive particles, electrically conductive particles, pigments, colorants, glass beads or bubbles, and the like, that are compatible with water-based systems based on a total weight of the adhesive composition. Any of these components, as well as any of the components listed above, can be used in various combinations, including two or more of each type of compound, to achieve desired results.

II. Methods of Making Adhesive Compositions

The adhesive compositions of the present invention may be prepared by mixing the adhesive composition components using conventional methods, as is well known by one skilled in the art. The components may be added simultaneously or sequentially; normally, low shear mixing equipment can be used. The components can be added in any order when making an adhesive composition.

In one exemplary method of making a one part system, the components can be added in the following order: the epoxy capsules, water, one or more thermoplastic binder resin dispersions or emulsions, the curative, and optional materials such as additives, cross-linking agents, thickeners, and fillers, if present. In one exemplary method of making a two part adhesive (parts A and B), the components of part A (i.e., amine-side) can include the following: curative, water, and optional materials such as additives, cross-linking agents, thickeners and fillers, if present. The components of part B (i.e., epoxy-side) can include the following: epoxy capsules, water, one or more thermoplastic binder resin dispersions or emulsions, and optional materials such as additives, cross-linking agents, thickeners and fillers, if present.

The adhesive compositions can be prepared as either one or two part adhesives. The one or two part adhesive compositions may be used directly after mixing or may be stored in suitable containers for future use. In compounding, or in customer use, additional water may be added to adjust the viscosity of the adhesive composition as desired.

The epoxy capsules used in the adhesive compositions of the present adhesive invention may be made by any known microencapsulation technique. One desired method of preparing the epoxy capsules of the present invention may be found in Example 1 below. Other microencapsulation techniques well known to those skilled in the art are disclosed in U.S. Patents Nos. 3,179,143; 3,642,937; and 3,746,068; Microcapsule Processing and Technology by Kondo (Marcel Dekker, 1979) and Microencapsulation (Encyclopedia of Polymer Science and Engineering, 2nd edition, Vol. 9, p. 724), the disclosures of which are hereby incorporated by reference.

III. Articles of Manufacture

The adhesive compositions of the present invention may be applied to a wide variety of substrates by any method known in the art. Suitable methods of application include, but are not limited to, spraying, gravure printing, dip coating (e.g., dipping the substrate into the adhesive composition), or flow coating (e.g., flowing the adhesive over the substrate). Substrates, which can be coated with the adhesive compositions of the present invention, include, but are not limited to, plastics, metals, ceramics, glass and cellulosic materials. Substrates may be in any configuration including, but not limited to, three-dimensional complex shapes, films, foils, foams, fabrics, tubes or pipes, etc. The adhesive compositions of the present invention are particularly useful as adhesive coatings on primed, bare or painted metal substrates such as stainless steel, aluminum, cold rolled steel and porcelainized steel. Moreover, the adhesive compositions of the present invention are particularly useful as adhesive coatings on mechanical fasteners, such as screws, bolts, nuts, pipe joints, and nails.

The amount of adhesive coating may vary depending on a number of factors including, but not limited to, the adhesive composition, the coating method, the substrate, and the particular application or use. Typically, a continuous adhesive coating is applied to at least a portion of a given substrate such that the coated areas have a basis coating weight of up to about 50 grams per square meter (gsm). When the adhesive is applied to a mechanical fastener, such as screws, bolts, nuts, pipe joints, and nails, the coating weight typically ranges from 0.05 grams to 0.50 grams, depending on the size of the fastener and how many of the threads are coated, with higher coating weights used on larger sized fasteners. However, it should be noted that the amount of adhesive coating is not limited in any way.

IV. Specific Uses

In one embodiment of the present invention, the above-described adhesive composition is coated onto at least a portion of a mechanical fastener. Suitable mechanical fasteners include, but are not limited to, screws, bolts, nuts, pipe joints, nails, etc. As the mechanical fastener is attached to a given object, the force exerted on the mechanical fastener causes the epoxy capsules to rupture. The epoxy resin and the curative intermix, initiating the curing process for the epoxy resin. The resulting mechanical fastener is mechanically, as well as, adhesively bonded to the substrate via the adhesive composition.

In a further embodiment of the present invention, the mechanical fastener comprises a bolt and nut assembly, wherein the threads of the bolt are coated with the above-described adhesive composition. It should be noted that the threads of the nut may also be coated with the adhesive composition. The resulting bolt and nut assembly has humidity resistance prior to use, as well as, acceptable bonding strength when attached to one another.

An exemplary coated mechanical fasteners is shown in FIG. **1**. Bolt **10** is coated with an adhesive composition **14**, which coats at least a portion of threads **12**. Adhesive composition **14** desirably comprises a polymeric binder matrix **18** having distributed therein epoxy capsules **20** (shown greatly enlarged), which contain a curable resin. A curing agent for the resin is also distributed throughout polymeric binder matrix **18**. As nut **22**, or equivalent mating threaded device, is threaded onto bolt **10**, some of the epoxy capsules **20** are ruptured by the shearing forces produced. The shearing forces caused by threading nut **22** onto bolt **10** also result in thorough mixing of the epoxy resin released from the epoxy capsules **20** with the curing agent, thus promoting cure of the released resin.

One method of measuring the humidity resistance of an adhesive composition on a mechanical fastener, such as a bolt and nut assembly, is to subject the

coated mechanical fastener to humid conditions for a period of time, attach the mechanical fastener to an object, let the adhesive cure, and then measure the adhesive bonding strength between the mechanical fastener and the object. The degree of humidity resistance of a given adhesive composition may be determined based of a minimum level of adhesive bonding strength and/or a percent retention of adhesive bonding strength relative to an original amount of adhesive bonding strength (i.e., the adhesive bonding strength of an adhesive composition that has not been subjected to the humid conditions). One such test is the "Humidity Stability Test" described below.

Desirably, the adhesive compositions of the present invention have a breakaway torque value (as measured by the "Breakaway Torque Test" described below) after being subjected to the Humidity Stability Test described below of at least about 5 N-m. In some embodiments, the adhesive compositions of the present invention have a breakaway torque value after being subjected to the Humidity Stability Test of at least about 10 N-m, at least about 15 N-m, or at least about 20 N-m.

The present invention is described above and further illustrated below by way of examples, which are not to be construed in any way as imposing limitations upon the scope of the invention. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present invention and/or the scope of the appended claims.

TEST EQUIPMENT

The following test equipment was used in the Test Methods and Examples described below.

Nuts and Bolts

Zinc-plated nuts and bolts (size 3/8 inch) were purchased from Adams Nut and Bolt, Maple Grove, MN, USA. The nuts and bolts were cleaned by immersing each nut or bolt in toluene for 10 minutes, draining and air-drying.

Torque Wrench

A "follow-up" torque wrench with dial readout was used (part no. TE50FUA, 3/8-inch drive, 0–600 in-lb scale, Snap-on Inc., Kenosha, WI, USA). The torque wrench was fitted with an appropriately sized 3/8-inch drive socket.

Nut driver

An air ratchet (Campbell Hausfeld, Harrison, OH, USA) was used to drive the nut onto the coated bolt. The air ratchet was driven by house compressed air. The nut driver was fitted with an appropriately sized 3/8-inch socket.

Zahn Cup

A #3 Zahn Type Viscosity Cup (Byk-Gardner, Columbia, MD) was used to measure adhesive viscosity. A digital stopwatch (VWR Scientific Products, South Plainfield, NJ) was used to measure the time needed to empty the cup (see Zahn Cup Viscosity Test Method below).

Brookfield Viscometer

Viscosity was measured using a Brookfield LDV-I+ viscometer with cylindrical spindles, L2 and L3. Viscosity readings were taken after the spindle had rotated in the solution for five minutes at room temperature (($20^{\circ}C \pm 2^{\circ}C$).

TEST METHODS

The following test methods were used to measure physical properties of exemplary uncured and cured adhesive compositions and articles containing the same.

Zahn Cup Viscosity

A #3 Zahn Type Viscosity Cup (Byk-Gardner, Columbia, MD, USA) was used to measure and adjust the adhesive viscosity prior to coating bolts with the adhesive. As described in ASTM Standard D 4212-99, a Zahn cup consists of a bullet-shaped stainless steel cup with an orifice in the bottom. The cup has a 12-inch loop handle to allow the cup to be dipped by hand into a liquid. At the center of this handle is a finger-ring for holding the cup in a vertical position during use. The size of the hole in the bottom of the Zahn cup is selected depending on the viscosity range to be tested. For example, the #3 Zahn cup has an orifice diameter of 0.38 cm and can be used to measure a viscosity in the range of 150 to 830 centistokes. In use, the cup is dipped into the liquid whose viscosity is to be measured, such that the cup is filled to the brim. The cup is quickly withdrawn from the liquid, and at the same time, a stopwatch is started to record the time. The stopwatch is stopped when there is a break in the liquid stream coming from the hole in the bottom of the cup. This time is recorded and is indicative of the liquid's viscosity at the measurement temperature ($20^{\circ}C \pm 2^{\circ}C$).

Brookfield Viscosity

The sample to be measured was added to an 8 oz. jar (236.6 ml). The 3L cylindrical spindle was attached to the Brookfield LDV-I+ viscometer and the spindle was inserted into the sample. Viscosity readings were taken 5 minutes after the spindle had rotated in the solution at 100 RPM, (room temperature was 20°C ± 2°C). See ASTM Standard D 2196-99 for more detail.

Initial Breakaway Torque Test

Nuts were applied to five coated bolts using the air-driven nut driver, such that the nut was completely engaged on the coated bolt. The nut-bolt assembly was cured at room temperature (25°C ± 2°C) for 24 hours. After cure, breakaway torque was measured using a follow-up torque wrench (described above). The nut-bolt assembly was held in place in a vise with the nut end up, and the torque wrench with drive socket was fitted over the nut. The needle on the dial of the torque wrench was set to zero, then the nut was loosened with a torque wrench in the counter-clockwise direction. The needle on the dial was deflected to the peak breakaway torque and this value was recorded. The average of five measurements was calculated and converted to N-m units.

Humidity Stability Test

Five coated bolts were placed into a humidity cabinet having a relative humidity of 100% and a temperature of 40°C. The bolts were exposed to the above-described conditions for four hours, such that the bolts were wet from condensed water. The bolts were then removed and cooled to room temperature for twenty four hours. Typically, the bolts were dry at this time. Nuts were then applied to the bolts and the nut-bolt assembly was allowed to cure at room temperature (25°C ± 2°C) for 24 hours. Breakaway torque was measured in the same way as the Initial Breakaway Torque Test described above. The average of five measurements was calculated and converted to N-m units. Breakaway torque values of 5.0 N-m or greater indicated an acceptable degree of humidity resistance.

EXAMPLES

The following examples were conducted using the materials shown in Table 1 below.

Table 1. Materials used in the examples

Trade Designation/ Material	Source	Description
ACRYSOL™ RM-8W	Rohm and Haas Company, Philadelphia, PA	Polyurethane thickener
AIRFLEX™ 430	Air Products, Inc., Philadelphia, PA	Poly vinyl chloride - polyvinyl acetate-ethylene terpolymer emulsion, % solids in water
AIRFLEX™ 4500	Air Products, Inc., Philadelphia, PA	Polyethylene-vinyl chloride copolymer emulsion, % solids in water
AIRFLEX™ 7200	Air Products, Inc., Philadelphia, PA	Polyvinyl acetate-ethylene copolymer emulsion, 73% solids in water
Aluminum Oxide C	Degussa Corporation Parsippany, NJ	Aluminum oxide powder
ANCAREZ™ AR550	Air Products, Inc., Allentown, PA	Solid epoxy dispersion, 55% solids in water
ANQUAMINE™ 401	Air Products, Inc., Allentown, PA	Aliphatic amine curing agent, 70% solids in water
BAYHYDROL 121	Bayer, Pittsburgh, PA	Polyurethane dispersion
CAB-O-SIL™ M5	Cabot Corporation, Tuscola, IL	Amorphous, fumed silica
Calcium carbonate, #10 white	Georgia Marble Company, Kennesaw, GA	Water-ground calcium carbonate filler, mean particle size 16 micrometers
CARBOSET CR-760	Noveon, Inc., Cleveland, OH	Styrene-acrylic copolymer emulsion, % solids in water
CORCAT™ P-600	EIT Company, Lake Wylie, SC	Polyethylenimine polymer, 33% solids in water
1,3-Dipiperidylpropane	Sigma-Aldrich Chemical Company, Milwaukee, WI	Aliphatic diamine curative
Epoxy capsules	Custom-made by 3M Canada Company, London, Ontario, Canada	Urea-melamine-formaldehyde shell filled with EPON™ 815C epoxy resin
FLEXBOND 325	Air Products, Inc., Philadelphia, PA	Polyvinyl acetate-acrylic copolymer emulsion, % solids in water
FOAMASTER™ 111	Cognis Corp, Cincinnati, OH	Anti-foam agent, oil based
Formaldehyde solution, (37 wt-%)	Hoechst-Celanese Chemical Company, Rock Hill, SC	Epoxy capsule reactant
HYBRIDUR 570	Air Products, Inc., Philadelphia, PA	Polyurethane-acrylic copolymer dispersion, % solids in water
HYCAR® 1578x1	Noveon, Inc., Cleveland, OH	Butadiene dispersion
Melamine (Melamine Aero Powder)	Cytec Industries, Wallingford, CT	Epoxy capsule reactant
MIN-U-GEL™	ITC, Inc., Hunt Valley, MD	Attapulgite clay thickener
MONOLITE™ Blue BG	Avecia Pigments and Additives, Wilmington, DE	Phthalocyanine Blue pigment (C. I. Pigment Blue, 15:3)
OCTOCURE 462	Tiarco Chemical , Dalton, GE	Zinc oxide cross-linker for rubber, aqueous dispersion

Trade Designation/ Material	Source	Description
OCTOCURE 590, T2000	Tiarco Chemical , Dalton, GE	Mixtures of zinc and sulfur compounds; cross-linker for rubber, aqueous dispersion
SANCURE 1601	Noveon, Inc., Cleveland, OH	Polyester dispersion, % solids in water
Sekesui S-LEC KW-1, KW-3	Summit Specialty Chemicals, US distributor for Sekesui Chemical Company, Ltd., Fort Lee, NJ	Water-soluble polyvinyl acetal resins (KW-1 = 18% solids in water, KW-3 =20% solids in water)
Sodium sulfate	IMC Chemicals, Inc., Trona, CA	Epoxy capsule reactant
Sulfuric acid (6M)	DuPont Chemicals, Wilmington, DE	Epoxy capsule reactant
Titanium dioxide T2020	Kronos, Inc., Houston, TX	Titanium dioxide pigment, rutile grade, alumina surface treatment
Triethanolamine (99%)	Dow Chemical Co., Midland, MI	Epoxy capsule reactant
Urea (industrial grade, 46% nitrogen)	Arcadian Fertilizer, L. P., Millington, TN	Epoxy capsule reactant
VANCRYL 937	Air Products, Inc., Philadelphia, PA	Polystyrene-acrylic copolymer emulsion, % solids in water
VINAC 285	Air Products, Inc., Philadelphia, PA	Polyvinyl acetate homopolymer dispersion, % solids in water
W-325 Mica	The C.P. Hall Company, Chicago, IL	Wet-ground Muscovite mica, 325 mesh
WITCOBOND® W-320	Crompton Corp., Middlebury, CT	Polyurethane dispersion

EXAMPLE 1

Preparation of Epoxy Capsules

A urea-melamine-formaldehyde precondensate was prepared by reacting a mixture of 956 g of 37 wt-% formaldehyde solution, 250 g of urea, 110 g of melamine and 8.6 g of triethanolamine for two hours 70°C. The reaction mixture was agitated during the reaction period using a six-blade turbine at 350 RPM, (Note: vessel configuration did not appear to be critical to the formation of the precondensate.) The resulting solution was aged for 18 hours at room temperature and diluted with 2103 g of distilled water to form a prepolymer solution.

1006 g of the prepolymer solution was added to a 4L stainless steel vessel equipped with baffles and a water jacket for temperature control and fitted with a 2 inch (5.1 cm) diameter, six-bladed turbine agitator 3 inch (7.6 cm) from the bottom of the reactor. The pH of the prepolymer solution was adjusted to 7.0 with 2.2 mL of 6M sulfuric acid and 10.1 g of sodium sulfate at room temperature. The batch temperature was set to 19°C and agitation was initiated at 700 RPM. 402 g of EPON™ 815C epoxy resin was added, and the agitation speed was increased to 1700 RPM. Stirring

continued for 30 minutes to ensure proper emulsification. 6M sulfuric acid was added at a rate of 1 mL per minute, until a pH target of 2.5 was reached, to initiate encapsulation. The reaction conditions were maintained at room temperature for one hour, at which time the temperature was increased to reach a target temperature of 70°C in 30 minutes and the pH was lowered further to 1.9. The reaction was allowed to proceed over 3.5 hours at which time the mixture was neutralized with 25 wt-% sodium hydroxide (OxyChem, Morristown, NJ). The slurry was allowed to cool to room temperature overnight, at which point the capsules were filtered and washed (3 times) with 400 mL of warm water (60°C).

In order to check the bulk stability of the capsules in water, 50 g of capsules were mixed with 50 g of CORCAT™ P-600. The mixture initially had a measured viscosity of 380 cps, which increased only slightly to 470 cps after eight weeks indicating bulk stability of the capsules in water.

EXAMPLE 2

Preparation of One-Part Formulations Without Fillers and with Multiple Binders

Fastener adhesive compositions were prepared using the components as shown in Table 1 above. The following procedure was followed to prepare the one-part formulations. Nine adhesive compositions were prepared using the components as shown in Tables 2-6 below. Into a plastic beaker were added the epoxy capsules, water, WITCOBOND™ W-320, AIRFLEX™ 7200, and HYCAR™ 1578x1. These components were mixed using an air-driven mixer with propeller blade. After mixing about one minute, the ANQUAMINE™ 401 and defoamer (FOAMASTER™ 111) were added and the sample was mixed until homogeneous (e.g., about 1 to 5 minutes, typically).

The mixture was diluted with water until the viscosity was in the range of 23-27 seconds as measured with a #3 Zahn cup. The viscosity of the adhesive solution was also measured using the Brookfield viscometer.

Table 2. Formulations for Examples 2-1 and 2-2

Formulation Component	Example 2-1				Example 2-2			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	100	39.68	70.0	50.54	100	38.17	70.0	50.80
ANQUAMINE™ 401	80	31.75	56.0	40.43	60	22.90	42.0	30.48
WITCOBOND® W-320	10	3.97	3.3	2.38	0	0.00	0.0	0.00
AIRFLEX™ 7200	10	3.97	7.2	5.20	20	7.63	14.4	10.45

HYCAR™ 1578x1	0	0.00	0.0	0.00	20	7.63	9.4	6.82
Water	50	19.84	0.0	0.00	60	22.90	0.0	0.00
FOAMASTER™ 111	2	0.79	2.0	1.44	2	0.76	2.0	1.45
TOTALS	252	100	138.5	100	262	100	137.8	100

Table 3. Formulations for Examples 2-3 and 2-4

Formulation Component	Example 2-3				Example 2-4			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	80	30.53	56.0	43.08	100	41.32	70.0	53.68
ANQUAMINE™ 401	80	30.53	56.0	43.08	40	16.53	28.0	21.47
WITCOBOND™ W-320	20	7.63	6.6	5.08	20	8.26	6.6	5.06
AIRFLEX™ 7200	0	0.00	0.0	0.00	20	8.26	14.4	11.04
HYCAR™ 1578x1	20	7.63	9.4	7.23	20	8.26	9.4	7.21
Water	60	22.90	0.0	0.00	40	16.53	0.0	0.00
FOAMASTER™ 111	2	0.76	2.0	1.54	2	0.83	2.0	1.53
TOTALS	262	100	130.0	100	242	100	137.8	100

Table 4. Formulations for Examples 2-5 and 2-6

Formulation Component	Example 2-5				Example 2-6			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	100	38.91	70.0	49.16	100	42.32	70.0	51.85
ANQUAMINE™ 401	80	31.13	56.0	39.33	60	24.79	42.0	31.11
WITCOBOND® W-320	0	0.00	0.0	0.00	20	8.26	6.6	4.89
AIRFLEX™ 7200	20	7.78	14.4	10.11	20	8.26	14.4	10.67
HYCAR™ 1578x1	0	0.00	0.0	0.00	0	0.00	0.0	0.00
Water	55	21.40	0.0	0.00	40	16.53	0.0	0.00
FOAMASTER™ 111	2	0.78	2.0	1.40	2	0.83	2.0	1.48
TOTALS	257	100	142.4	100	242	100	135.0	100

Table 5. Formulation for Example 2-7 and 2-8

Formulation Component	Example 2-7				Example 2-8			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	80	31.75	56.0	41.48	80	34.48	56.0	42.94
ANQUAMINE™ 401	80	31.75	56.0	41.48	60	25.86	42.0	32.21
WITCOBOND™ W-320	20	7.94	6.6	4.89	20	8.62	6.6	5.06
AIRFLEX™ 7200	20	7.94	14.4	10.67	20	8.62	14.4	11.04
HYCAR™ 1578x1	0	0.00	0.0	0.00	20	8.62	9.4	7.21
Water	50	19.84	0.0	0.00	30	12.93	0.0	0.00
FOAMASTER™ 111	2	0.79	2.0	1.48	2	0.86	2.0	1.53
TOTALS	252	100	135.0	100	232	100	130.4	100

Table 6. Formulation for Example 2-9

Formulation Component	Example 2-9			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	90.9	39.15	63.6	47.23
ANQUAMINE™ 401	70.9	30.53	49.6	36.84
WITCOBOND® W-320	12.8	5.51	4.2	3.14
AIRFLEX™ 7200	12.8	5.51	9.2	6.84
HYCAR™ 1578x1	12.8	5.51	6.0	4.47
Water	30	12.92	0.0	0.00
FOAMASTER™ 111	2	0.86	2.0	1.48
TOTALS	232.2	100	134.7	100

Examples 2-1 to 2-9 were tested for initial breakaway torque and for humidity resistance using the Humidity Stability Test as described above. The adhesive was coated onto bolts by dipping so that approximately three quarters of the threads were coated. Excess adhesive was removed by scraping the bolt against the container approximately ten times such that the dried adhesive coating weight for the 10 coated bolts averaged 0.15 ± 0.05 g per bolt. The bolts were dried in a 70°C oven for 1 hour and cooled to room temperature. When cooled, nuts were applied using an air pressure driven nut driver. Of the ten bolts coated per sample, five were used to measure initial

breakaway strength (no humidity exposure), and five bolts were used for the Humidity Stability Test.

The Initial Breakaway Torque and Humidity Stability Test results are given below in Table 7. All Examples 2-1 to 2-9 had acceptable humidity resistance by exhibiting a breakaway torque value of greater than 5.0 N-m.

Table 7: Evaluation for Examples 2-1 to 2-9

Property	Example								
	2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8	2-9
Brookfield viscosity (centapoise)	100	223	198	201	252	250	244	294	265
Zahn cup #3 viscosity (sec)	26	26	25	24	24	25	25	26	25
Initial Breakaway Torque Test – 24 hour cure (N-m)	16.1	21.4	18.5	21.2	19.0	22.8	12.1	17.8	19.8
Humidity Stability Test (N-m)	9.3	8.3	12.1	13.1	11.4	14.7	12.9	7.1	9.1

EXAMPLE 3

Preparation of One-Part Formulations Without Fillers and with a Single Binder

Fastener adhesive compositions were prepared using the components as shown in Table 1 above. The following procedure was followed to prepare the one-part formulations. Twelve adhesive compositions were prepared using the components as shown in Tables 8 and 10 below. Into a plastic beaker were added the epoxy capsules, water, and a single binder. These components were mixed using an air-driven mixer with propeller blade. After mixing about one minute, the curative amine was added and the sample was mixed about one minute until homogeneous. The examples were tested for Initial Breakaway Torque and Humidity Stability as shown in Tables 9 and 11.

Table 8: Formulations for Examples 3-1 to 3-6

	Examples					
	3-1	3-2	3-3	3-4	3-5	3-6
Epoxy capsules (pph)	40.0	40.0	40.0	40.0	40.0	40.0
ANQUAMINE™ 401 (pph)	30.0	30.0	30.0	30.0	30.0	30.0
AIRFLEX™ 430 (pph)	15.0					
AIRFLEX™ 4500 (pph)		15.0				

AIRFLEX™ 7200 (pph)			15.0			
BAYHYDROL™ 121 (pph)				15.0		
CARBOSET CR-760 (pph)					15.0	
FLEXBOND 325 (pph)						15.0
Water (pph)	31.0	31.3	30.0	30.0	25.1	23.0

Table 9: Evaluation of Examples 3-1 to 3-6

Property	Example					
	3-1	3-2	3-3	3-4	3-5	3-6
Zahn cup #3 viscosity (sec)	23	23	24	22	22	24
Initial Breakaway Torque Test – 24 hour cure (N-m)	32.5	29.6	28.3	24.0	22.8	27.4
Humidity Stability Test (N-m)	38.9	36.1	22.3	11.9	29.1	45.3

Table 10: Formulations for Examples 3-7 to 3-12

	Example					
	3-7	3-8	3-9	3-10	3-11	3-12
Epoxy capsules (pph)	40.0	40.0	40.0	40.0	40.0	40.0
ANQUAMINE™ 401 (pph)	30.0	30.0	30.0	30.0	30.0	30.0
HYBRIDUR 570 (pph)	15.0					
HYCAR™ 1578x1 (pph)		15.0				
SANCURE 1601 (pph)			15.0			
VANCRYL 939 (pph)				15.0		
VINAC 285 (pph)					15.0	
WITCOBOND W-320 (pph)						15.0
Water	29.0	25.2	25.0	30.0	25.0	25.2

Table 11: Evaluation of Examples 3-7 to 3-12

Property	Example					
	3-7	3-8	3-9	3-10	3-11	3-12
Zahn cup #3 viscosity (sec)	22	22	23	24	22	22
Initial Breakaway Torque Test – 24 hour cure (N-m)	25.3	21.7	28.1	21.7	28.3	28.1
Humidity Stability Test (N-m)	27.0	18.3	26.4	31.7	20.4	19.3

EXAMPLE 4

Preparation of One-Part Formulations With Fillers

Fastener adhesive compositions were prepared using the components as shown in Table 1 above. The following procedure was followed to prepare the one-part formulations. Twelve adhesive compositions were prepared using the components as shown in Tables 12-17 below. Into a plastic beaker were added the epoxy capsules, water, WITCOBOND™ W-320, and AIRFLEX™ 7200. These components were mixed using an air-driven mixer with propeller blade. After mixing about one minute, the ANQUAMINE™ 401 and defoamer (FOAMASTER™ 111) were added and the sample was mixed for one minute. At that time, the titanium dioxide, calcium carbonate and mica fillers were added and the sample was mixed until homogeneous (about two minutes).

The mixture was diluted with water until the viscosity was in the range of 23-27 seconds as measured with a #3 Zahn cup. The viscosity of the adhesive solution was also measured with a Brookfield viscometer.

Table 12. Formulation of Examples 4-1 and 4-2

Formulation Component	Example 4-1				Example 4-2			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	95	40.95	66.5	48.07	90	36.44	63.0	44.46
ANQUAMINE™ 401	57	24.57	39.9	28.84	54	21.86	37.8	26.68
WITCOBOND® W-320	19	8.19	6.3	4.53	18	7.29	5.9	4.19
AIRFLEX™ 7200	19	8.19	13.7	9.89	18	7.29	13.0	9.15
Titanium dioxide	10	4.31	10.0	7.23	0	0.00	0.0	0.00
Calcium carbonate	0	0.00	0.0	0.00	0	0.00	0.0	0.00

Mica	0	0.00	0.0	0.00	20	8.10	20.0	14.11
Water	30	12.93	0.0	0.00	45	18.22	0.0	0.00
FOAMASTER™ 111	2	0.86	2.0	1.45	2	0.81	2.0	1.41
TOTALS	232	100	138.4	100	247	100	141.7	100

Table 13: Formulation for Example 4-3 and 4-4

Formulation Component	Example 4-3				Example 4-4			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	81.6	33.72	57.1	38.77	90	38.79	63.0	44.46
ANQUAMINE™ 401	49	20.25	34.3	23.28	54	23.28	37.8	26.68
WITCOBOND™ W-320	16.3	6.74	5.4	3.65	18	7.76	5.9	4.19
AIRFLEX™ 7200	16.3	6.74	11.7	7.97	18	7.76	13.0	9.15
Titanium dioxide	15.6	6.45	15.6	10.59	20	8.62	20.0	14.11
Calcium carbonate	10.6	4.38	10.6	7.19	0	0.00	0.0	0.00
Mica	10.6	4.38	10.6	7.19	0	0.00	0.0	0.00
Water	40	16.53	0.0	0.00	30	12.93	0.0	0.00
FOAMASTER™ 111	2	0.83	2.0	1.36	2	0.86	2.0	1.41
TOTALS	242	100	147.3	100	232	100	141.7	100

Table 14: Formulation for Example 4-5 and 4-6

Formulation Component	Example 4-5				Example 4-6			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	90	37.19	63.0	44.46	90	37.19	63.0	44.46
ANQUAMINE™ 401	54	22.31	37.8	26.68	54	22.31	37.8	26.68
WITCOBOND™ W-320	18	7.44	5.9	4.19	18	7.44	5.9	4.19
AIRFLEX™ 7200	18	7.44	13.0	9.15	18	7.44	13.0	9.15
Titanium dioxide	10	4.13	10.0	7.06	0	0.00	0.0	0.00
Calcium carbonate	0	0.00	0.0	0.00	10	4.13	10.0	7.06
Mica	10	4.13	10.0	7.06	10	4.13	10.0	7.06
Water	40	16.53	0.0	0.00	40	16.53	0.0	0.00
FOAMASTER™ 111	2	0.83	2.0	1.41	2	0.83	2.0	1.41
TOTALS	242	100	141.7	100	242	100	141.7	100

Table 15: Formulations for Examples 4-7 and 4-8

Formulation Component	Example 4-7					Example 4-8			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%		Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	95	39.26	66.5	48.07		95	39.26	66.5	48.07
ANQUAMINE™ 401	57	23.55	39.9	28.84		57	23.55	39.9	28.84
WITCOBOND™ W-320	19	7.85	6.3	4.53		19	7.85	6.3	4.53
AIRFLEX™ 7200	19	7.85	13.7	9.89		19	7.85	13.7	9.89
Titanium dioxide	0	0.00	0.0	0.00		0	0.00	0.0	0.00
Calcium carbonate	0	0.00	0.0	0.00		10	4.13	10.0	7.23
Mica	10	4.13	10.0	7.23		0	0.00	0.0	0.00
Water	40	16.53	0.0	0.00		40	16.53	0.0	0.00
FOAMASTER™ 111	2	0.83	2.0	1.45		2	0.83	2.0	1.45
TOTALS	242	100	138.4	100		242	100	138.4	100

Table 16: Formulations for Examples 4-9 and 4-10

Formulation Component	Example 4-9					Example 4-10			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%		Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	75	30.99	52.5	34.60		85	35.86	59.5	41.02
ANQUAMINE™ 401	45	18.60	31.5	20.76		51	21.52	35.7	24.61
WITCOBOND™ W-320	15	6.20	5.0	3.26		17	7.17	5.6	3.87
AIRFLEX™ 7200	15	6.20	10.8	7.12		17	7.17	12.2	8.44
Titanium dioxide	20	8.26	20.0	13.18		10	4.22	10.0	6.89
Calcium carbonate	20	8.26	20.0	13.18		20	8.44	20.0	13.79
Mica	10	4.13	10.0	6.59		0	0.00	0.0	0.00
Water	40	16.53	0.0	0.00		35	14.77	0.0	0.00
FOAMASTER™ 111	2	0.83	2.0	1.32		2	0.84	2.0	1.38
TOTALS	242	100	151.8	100		237	100	145.1	100

Table 17: Formulation for Examples 4-11 and 4-12

Formulation Component	Example 4-11				Example 4-12			
	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%	Parts By Wt (pbw)	Wet Wt-%	Solids Content (pbw)	Dry Wt-%
Epoxy capsules	90	37.19	63.0	44.46	75	30.99	52.5	34.60
ANQUAMINE™ 401	54	22.31	37.8	26.68	45	18.60	31.5	20.76
WITCOBOND™ W-320	18	7.44	5.9	4.19	15	6.20	5.0	3.26
AIRFLEX™ 7200	18	7.44	13.0	9.15	15	6.20	10.8	7.12
Titanium dioxide	0	0.00	0.0	0.00	20	8.26	20.0	13.18
Calcium carbonate	20	8.26	20.0	14.11	20	8.26	20.0	13.18
Mica	0	0.00	0.0	0.00	10	4.13	10.0	6.59
Water	40	16.53	0.0	0.00	40	16.53	0.0	0.00
FOAMASTER™ 111	2	0.83	2.0	1.41	2	0.83	2.0	1.32
TOTALS	242	100	141.7	100	242	100	151.8	100

Examples 4-1 and 4-12 were tested for humidity resistance using the Humidity Stability Test as described above. Bolts were coated with adhesive composition as described in Example 2. The test results are given below in Tables 18-19.

Table 18: Evaluation of Examples 4-1 to 4-7

Property	Example						
	4-1	4-2	4-3	4-4	4-5	4-6	4-7
Brookfield viscosity (centapoise)	320	258	410	480	280	295	285
Zahn cup #3 viscosity (sec)	25	25	25	26	24	26	24
Breakaway Torque Test – 24 hour cure (N-m)	26.8	21.6	36.5	37.1	28.1	26.5	26.7
Humidity Stability Test (N-m)	20.4	15.4	20.4	20.4	21.5	14.7	15.1

Table 19: Evaluation of Examples 4-8 to 4-12

Property	Example				
	4-8	4-9	4-10	4-11	4-12
Brookfield viscosity (centapoise)	295	455	253	325	455
Zahn cup #3 viscosity (sec)	24	27	25	25	26
Breakaway Torque Test – 24 hour cure (N-m)	25.8	37.8	38.1	38.1	48.9
Humidity Stability Test (N-m)	8.6	8.8	6.6	6.6	22.4

As can be seen in Tables 18-19, all of examples 4-1 to 4-12 had acceptable humidity resistance by exhibiting a breakaway torque value of greater than 5.0 N-m.

EXAMPLE 5

Preparation of Two-Part Formulations With Fillers

Eight adhesive compositions were prepared using the components as shown in Tables 20-21 below. The following procedure was followed to prepare the two-part formulations.

For Part A: into a plastic beaker was added the ANQUAMINE™ 401, and water. These components were mixed using an air-driven mixer with propeller blade. After mixing about one minute, the MONOLITE Blue BG, Aluminum Oxide C and FOAMASTER™ 111 were added and the sample was mixed for one minute. At that time, the titanium dioxide, calcium carbonate and mica fillers were added and the sample was mixed until homogeneous (about two minutes).

For Part B: into a plastic beaker were added the epoxy capsules, water, WITCOBOND™ W-320, and AIRFLEX™ 7200. These components were mixed using an air-driven mixer with propeller blade. After mixing about one minute, the ACRYSOL™ RM-8W, MIN-U-GEL 400, FOAMASTER™ 111, OCTOCURE materials, and ANCAREZ AR550 were added and the sample was mixed until homogeneous (about two minutes).

Part A + Part B: 150 g of Part A and 150 g of Part B were mixed together by hand using a stirring rod, followed by dilution with de-ionized water so that the viscosity was 23 seconds as measured with a #3 Zahn cup.

Table 20: Formulation of Examples 5-1 to 5-4

Ingredients	Formulation (Amount in parts by weight, pbw)							
	Ex. 5-1		Ex. 5-2		Ex. 5-3		Ex. 5-4	
	A	B	A	B	A	B	A	B
Epoxy capsules	50		50		50		50	
ANQUAMINE™ 401		22.5		22.5		22.5		22.5
WITCOBOND™ W-320	5		5		7.5		7.5	
AIRFLEX™ 7200	10		10		7.5		7.5	
ACRYSOL™ RM-8W	1	0.5	1	0.5	1	0.5	1	0.5
MIN-U-GEL™ 400	0.25		0.25		0.25		0.25	
Water	20	12.5	20	12.5	20	12.5	20	12.5
Aluminum Oxide C		0.5		0.5		0.5		0.5
FOAMASTER™ 111	1	1	1	1	1	1	1	1
Titanium dioxide		20		20		20		20
Calcium carbonate				5				5
Mica		5		5		5		5

Table 21: Formulations for Examples 5-5 to 5-8

Ingredients	Formulation (Amount in parts by weight, pbw)							
	Ex. 5-5		Ex. 5-6		Ex. 5-7		Ex. 5-8	
	A	B	A	B	A	B	A	B
Epoxy capsules	50		50		50		50	
ANQUAMINE™ 401		22.5		22.5		22.5		22.5
WITCOBOND™ W-320	5							
AIRFLEX™ 7200	10							
ACRYSOL™ RM-8W	1	0.5		0.5		0.5		0.5
MIN-U-GEL™ 400	0.25							
ANCAREZ™ AR550	10							
OCTOCURE 462			0.5					
OCTOCURE 590					0.5			
OCTOCURE T2000							0.5	
Water	20	12.5		12.5		12.5		12.5
MONOLITE™ Blue BG		0.5		0.5		0.5		0.5
Aluminum Oxide C		0.5		0.5		0.5		0.5
FOAMASTER™ 111	1	1		1		1		1
Titanium dioxide		20		20		20		20
Mica		5		5		5		5

Examples 5-1 to 5-8 were tested for humidity resistance using the Humidity Stability Test as described above. Bolts were coated with adhesive composition as described in Example 2. The test results are given below in Table 22.

Table 22: Evaluation of Examples 5-1 to 5-8

Property	Examples							
	5-1	5-2	5-3	5-4	5-5	5-6	5-7	5-8
Zahn cup #3 viscosity (sec)	23	23	23	23	23	23	23	23
Breakaway Torque Test – 24 hour cure (N-m)	24.7	21.7	28.7	16.1	15.6	13.7	13.6	14.2
Humidity Stability Test (N-m)	18.6	17.0	16.4	14.8	10.2	11.8	13.9	11.9

As can be seen in Table 22, all of Examples 5-1 to 5-8 had acceptable humidity resistance by exhibiting a breakaway torque value of greater than 5.0 N-m.

EXAMPLE 6

Preparation of Two-Part Formulations With Fillers

Two adhesive compositions were prepared using the components as shown in Table 23 below. The procedure as described in Example 4 was followed to prepare the two-part formulations.

Table 23: Preparation of Examples 6-1 and 6-2

Ingredients	Formulation (Amount in parts by weight, pbw)			
	Example 6-1		Example 6-2	
	A	B	A	B
Epoxy capsules	50.0		50.0	
ANQUAMINE™ 401		22.5		22.5
WITCOBOND™ W-320	5.0		5.0	
OCTOCURE 590			1.5	
AIRFLEX™ 7200	10.0		10.0	
ACRYSOL™ RM-8W	1.0	0.5	1.0	0.5
MIN-U-GEL™ 400	0.25		0.25	
Water	20		20	
MONOLITE™ Blue BG		0.5		0.5
FOAMASTER™ 111	1.0	1.0	1.0	1.0
Aluminum Oxide C		0.5		0.5
Titanium dioxide		20.0		20.0
Mica		5.0		5.0

Total parts by weight, wet weight percent, solids content and dry weight percent for Examples 6-1 and 6-2 are given in Table 24 below. Evaluation results are also included in Table 24 for these examples.

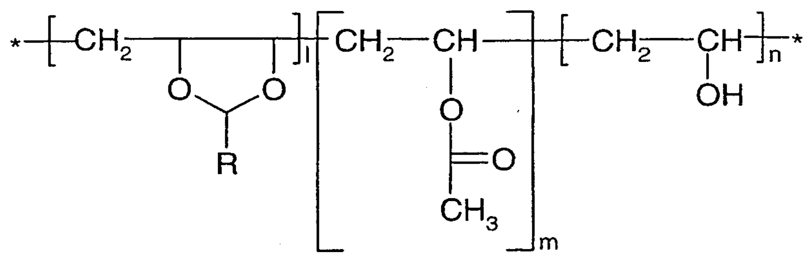
Table 24. Formulations and Properties for Examples 6-1 and 6-2

Ingredients	Example 6-1				Example 6-2			
	Parts By Wt (pbw)	Wet Wt%	Percent Solids (%)	Dry Wt %	Parts By Wt (pbw)	Wet Wt%	Percent Solids (%)	Dry Wt%
Epoxy capsules	50.0	36.43	25.50	39.69	50.0	36.04	25.23	39.21
ANQUAMINE™ 401	22.5	16.39	11.48	17.86	22.5	16.22	11.35	17.65
WITCOBOND™ W-320	5.0	3.64	1.20	1.87	5.0	3.60	1.19	1.85
OCTOCURE 590	0.0	0.0	0.0	0.0	1.5	1.08	0.78	1.21
OCTOCURE T2000	1.5	1.08	0.78	1.21	0.0	0.0	0.0	0.0
AIRFLEX™ 7200	10.0	7.29	5.25	8.17	10.0	7.21	5.19	8.07
ACRYSOL™ RM-8W	1.5	1.09	0.23	0.37	1.5	1.08	0.23	0.36
MIN-U-GEL™ 400	0.25	0.18	0.18	0.28	0.25	0.18	0.18	0.28
Water	20.0	14.57	0.00	0.00	20.0	14.41	0.00	0.00
MONOLITE™ Blue BG	0.5	0.36	0.36	0.57	0.5	0.36	0.36	0.56
FOAMASTER™ 111	2.0	1.46	1.46	2.27	2.0	1.44	1.44	2.24
Aluminum Oxide C	0.5	0.36	0.36	0.57	0.5	0.36	0.36	0.56
Titanium dioxide	20.0	14.57	14.57	22.68	20.0	14.41	14.41	22.41
Mica	5.0	3.64	3.64	5.67	5.0	3.60	3.60	5.60
TOTALS	137.3	100	64.23	100	138.8	100	64.32	100
Zahn cup #3 viscosity (sec)	23				23			
Breakaway Torque Test – 24 hour cure (N-m)	14.2				13.6			
Humidity Stability Test (N-m)	11.9				13.9			

COMPARATIVE EXAMPLE 7

Preparation of Adhesive Formulations from U.S. Patent No. 5,283,266

Comparative fastener adhesive compositions were prepared using the following polyacetal resins of the following formula:



The variables l, m, n, and R are specified for each comparative example in Table 25 below.

Table 25. Polyacetal Resins

Polyacetal Water Soluble Resins	US 5,283,266 Ex. 1	US 5,283,266 Ex. 2	US 5,283,266 Ex. 3	Sekesui S-LEC KW-1	Sekesui S-LEC KW-3
Acetal linkage, l	5	10	15	9 ± 2	30 ± 3
Acetyl linkage, m	15	10	3	12	12
Hydroxyl linkage, n	80	80	82	79	58
m+n	95	90	85	91	88
R	butyl	ethyl	methyl	methyl	methyl

Adhesive formulations were prepared according to the Examples in U.S. Patent No. 5,283,266 using epoxy capsules made as described in Example 1 and commercially available Sekesui resins shown in Table 25 above. Comparative example formulations 7-1 to 7-8 are given in Table 26 below. The samples were prepared by addition of epoxy capsules into a plastic beaker followed by addition of water, curative and polyacetal resin. These components were blended together for one minute using an air-powered mixer with propeller blade. After initial mixing, the silica filler was added and blended into the mixture for up to two minutes. In the case of comparative examples 7-1 and 7-5, the resultant mixtures were dough-like in consistency and could not be easily mixed. Because of this, additional water was added and the samples mixed to a paste consistency (comparative examples 7-2 and 7-6). In the case of comparative examples 7-4 and 7-8, the resultant mixture was a thick gooey mass in water, which could not be mixed together.

Table 26. Comparative Example Formulations

Ingredients	Formulation (Amount in parts by weight, pbw)							
	7-1	7-2	7-3	7-4	7-5	7-6	7-7	7-8
US 5,283,266 example number	1	1 + Water	2	3	1	1 + Water	2	3
Epoxy capsules	20	20	10	5	20	20	10	5
Sekesui KW-1 polyacetal resin	3	3	5	15	0	0	0	0
Sekesui KW-3 polyacetal resin	0	0	0	0	3	3	5	15
CAB-O-SIL™ M5 silica powder	5	5	3	0	5	5	3	0
Water to mix	8	53	25	26	8	53	25	26
1,3-dipiperidylpropane curative	14	14	7	4	14	14	7	4

The adhesive compositions of comparative examples 7-1 to 7-8 were coated onto bolts as described in Example 2. As described above, additional water had to be added to comparative examples 7-2 and 7-6 to enable the compositions to be coated onto bolts. Comparative examples 7-1 and 7-5 were not usable.

Because the comparative example adhesives were pastes, the excess adhesive was removed by running a finger over the bolt surface until no more excess adhesive was removed, such that the dried adhesive coating weight for the 10 coated bolts averaged 0.15 $\pm$ 0.05 g per bolt. The test results are given below in Table 27. Comparative examples 7-2, 7-3, 7-6, and 7-7 had unacceptable humidity resistance, exhibiting a breakaway torque value of less than 5.0 N-m.

Table 27. Humidity Stability Test Results For Comparative Samples 7-1 to 7-8

Property	Comparative Example							
	7-1	7-2	7-3	7-4	7-5	7-6	7-7	7-8
Viscosity (poise)	Nd	1250	4000	Nd	Nd	930	4070	Nd
Consistency	Dough	Thin paste	Thick paste	Thick goo sep'd from water	Dough	Thin paste	Thick paste	Thick goo sep'd from water
Breakaway Torque Test (24 hour cure at room temp.) (N-m)	Nd	6.8	15.3	Nd	Nd	6.5	17.4	Nd
Humidity Stability Test (N-m)	Nd	1.7	1.9	Nd	Nd	1.2	1.5	Nd

Sep'd = separated

Nd = not determined

While the specification has been described in detail with respect to specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.

WHAT IS CLAIMED IS:

1. A water-based adhesive composition comprising:

epoxy capsules comprising an outer shell material and an encapsulated material surrounded by the outer shell material, said encapsulated material comprising an epoxy resin;

a non-volatile amine curative; and

a binder system, wherein the binder system comprises at least one water-insoluble polymer.

2. The water-based adhesive composition of claim 1, wherein the binder system is selected from ethylene-vinyl acetate copolymer emulsions, ethylene-vinyl chloride copolymer emulsions, vinyl acetate-ethylene-vinyl chloride copolymer emulsions, acrylate-vinyl acetate-ethylene copolymer emulsions, vinyl acrylic emulsions, acrylic emulsions, vinyl acetate-acrylic copolymer emulsions, styrene-acrylic copolymer emulsions, vinyl chloride-vinyl acetate-ethylene terpolymer emulsions, vinyl acetate homopolymer emulsions, polyester dispersions, polyurethane dispersions, acrylic-urethane dispersions, butadiene dispersions, butadiene-styrene copolymer dispersions, and combinations thereof.

3. The water-based adhesive composition of claim 1, wherein the binder system is selected from ethylene-vinyl acetate copolymer emulsions, polyurethane dispersions, and butadiene dispersions, and combinations thereof.

4. The water-based adhesive composition of claim 1, wherein the outer shell material comprises a urea-formaldehyde-melamine material.

5. The water-based adhesive composition of claim 1, wherein the epoxy capsules have a median particle size of about 20 to about 120 micrometers.

6. The water-based adhesive composition of claim 1, wherein the epoxy resin comprises a diglycidyl ester of Bisphenol A, a hydrogenated Bisphenol A epichlorohydrin based epoxy resin, an aliphatic epoxy resin, or a combination thereof.

7. The water-based adhesive composition of claim 1, wherein the encapsulated material further comprises an epoxy diluent.

8. The water-based adhesive composition of claim 1, wherein the epoxy capsules are present in an amount of about 20 to about 60 weight percent, the binder system is present in an amount of at least 5 to about 25 weight percent, and the amine curative is present in an amount of about 1 to about 30 weight percent based on the weight of the adhesive composition.

9. The water-based adhesive composition of claim 1, further comprising an inorganic or polymeric filler material.

10. The water-based adhesive composition of claim 1, wherein the amine curative is a polymeric material.

11. An article comprising:

a) a substrate having an outer surface; and

b) an adhesive composition on at least a portion of the outer surface of the substrate, said adhesive composition comprising:

i) epoxy capsules comprising an outer shell material and encapsulated material surrounded by the outer shell material, said encapsulated material comprising an epoxy resin;

ii) a non-volatile amine curative; and

iii) a binder system, wherein the binder system comprises at least one water-insoluble polymer.

12. The article of claim 11, wherein the substrate is a three-dimensional shape, a film, a foil, a fabric, a tube, a pipe, or a mechanical fastener.

13. The article of claim 12, wherein the substrate is a mechanical fastener.

14. The article of claim 13, wherein the mechanical fastener comprises a screw, bolt, nut, nail, pipe joint, or a bolt/nut assembly.

15. The article of claim 13, wherein the mechanical fastener comprises a bolt, and wherein the bolt having the reaction product of the adhesive composition thereof and a subsequently attached nut exhibit a breakaway torque value greater than about 5 N-m following a Humidity Resistance Test.

16. The article of claim 15, wherein the breakaway torque value is greater than about 10 N-m following a Humidity Resistance Test.

17. The article of claim 11, wherein the binder system is selected from ethylene-vinyl acetate copolymer emulsions, ethylene-vinyl chloride copolymer emulsions, vinyl acetate-ethylene-vinyl chloride copolymer emulsions, acrylate-vinyl acetate-ethylene copolymer emulsions, vinyl acrylic emulsions, acrylic emulsions, vinyl acetate-acrylic copolymer emulsions, styrene-acrylic copolymer emulsions, vinyl chloride-vinyl acetate-ethylene terpolymer emulsions, vinyl acetate homopolymer emulsions, polyester dispersions, polyurethane dispersions, acrylic-urethane dispersions, butadiene dispersions, butadiene-styrene copolymer dispersions, and combinations thereof.

18. The article of claim 11, wherein the epoxy capsules are present in an amount of about 20 to about 60 weight percent, the binder system is present in an amount of about 5 to about 25 weight percent, and the amine curative is present in an amount of about 1 to about 30 weight percent based on the weight of the adhesive composition.

19. The article of claim 11, wherein the binder system is selected from ethylene-vinyl acetate copolymer emulsions, polyurethane dispersions, and butadiene dispersions, and combinations thereof.

20. The article of claim 11, wherein the adhesive composition further comprises an inorganic or polymeric filler, a thickener, or a combination thereof.

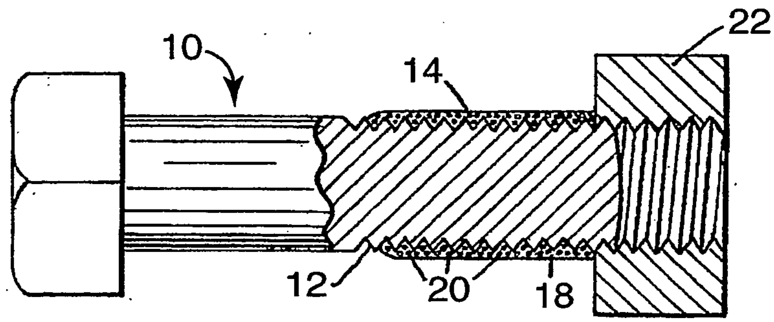


Fig. 1

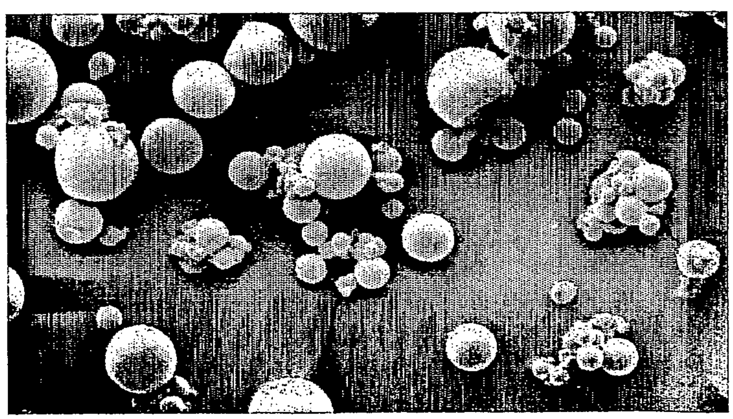


Fig. 2

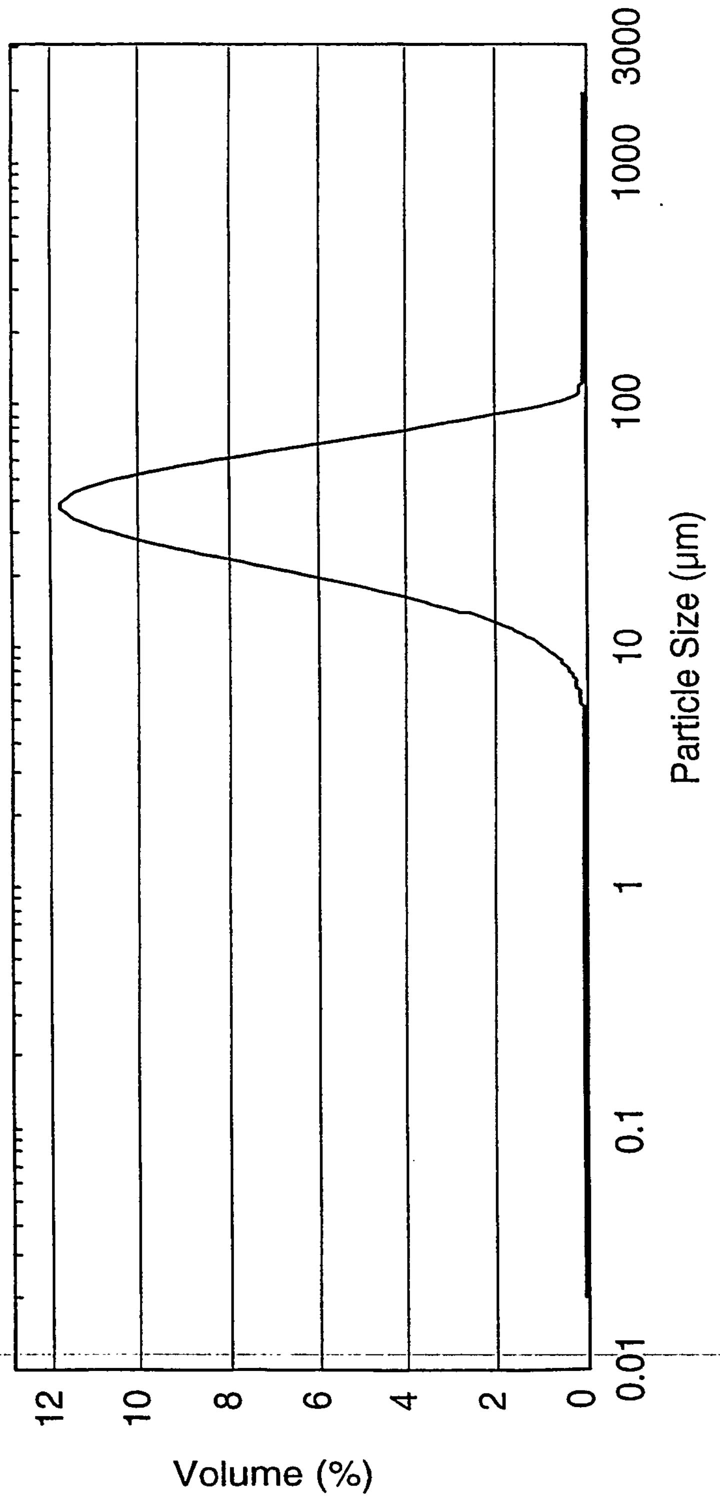


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/19505

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09J129/14 C09J163/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 543 675 A (THREE BOND CO LTD) 26 May 1993 (1993-05-26) page 2, line 25 -page 3, line 18 abstract; claims 1-3; examples 1-5 -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 October 2003	30/10/2003

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/19505

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